

Correlation Effects in Li/Na_xCoO₂

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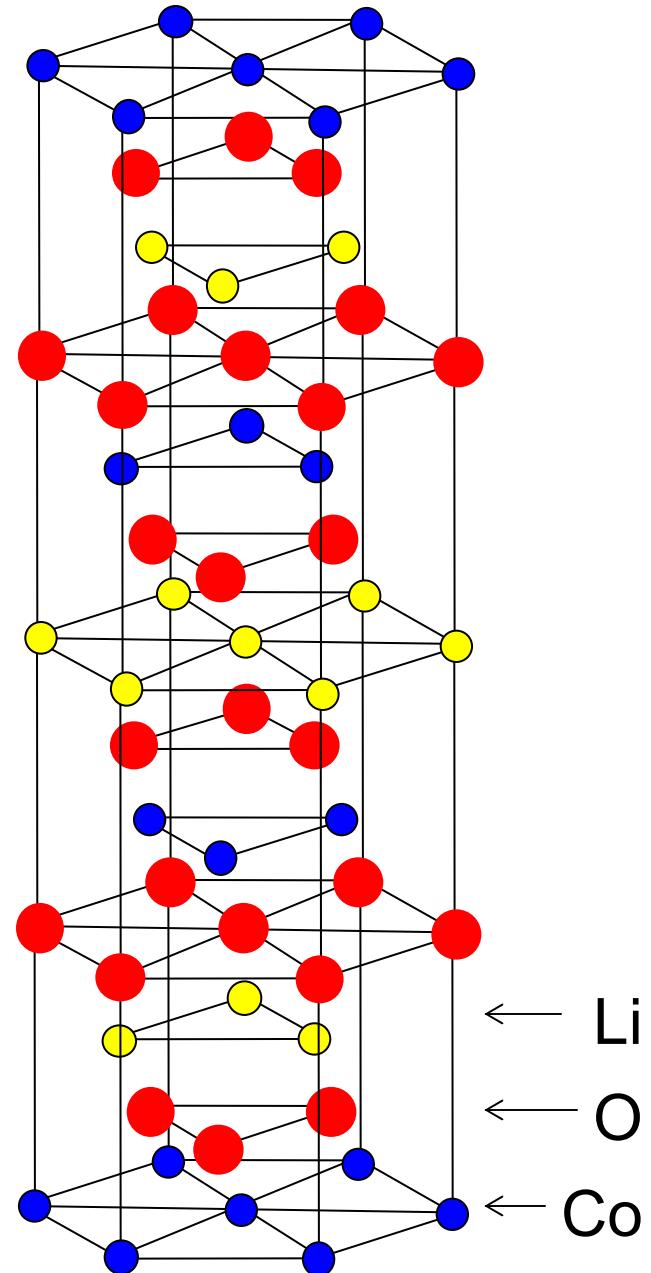
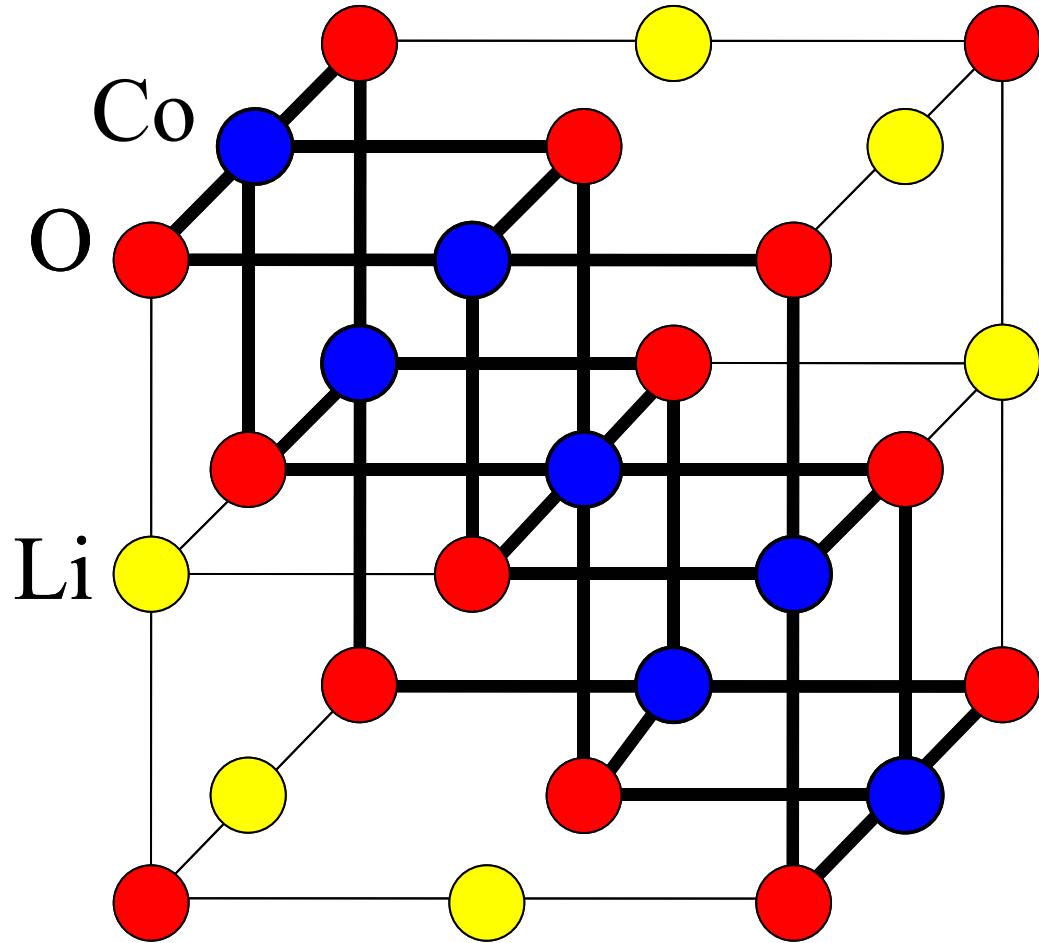
Introduction

- Li_xCoO_2 – Primary cathode material in rechargeable Li batteries.
- Na_xCoO_2 – Hydration gives superconductor
- Layered triangular lattices
- Low spin $\text{Co}^{(4-x)+}$ $\longrightarrow t_{2g}^{5+x}$
- How does doping effect the system?
- Do Oxygen and e_g orbitals play any role?

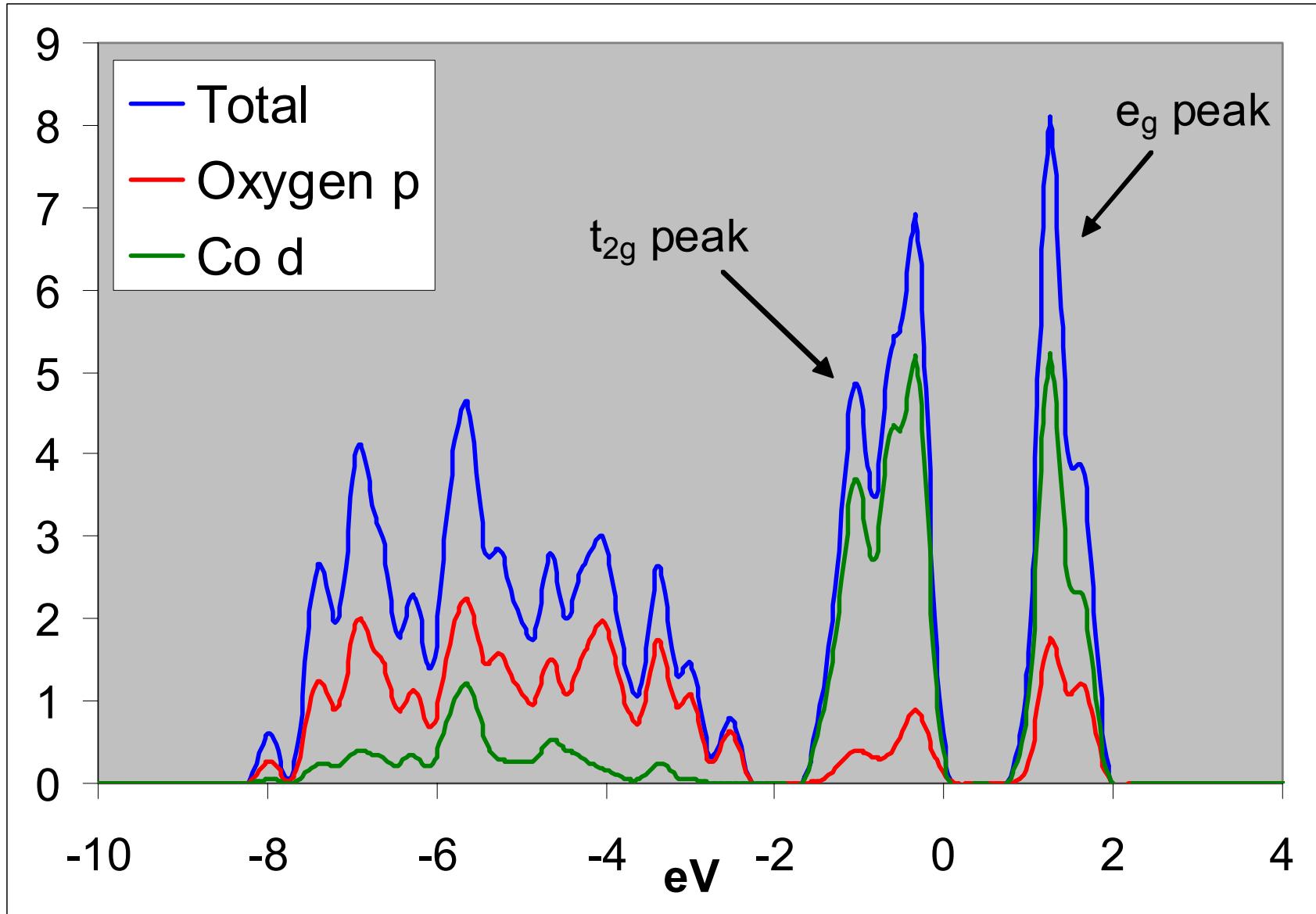
Methodology

- Use LDA to determine changes in the ground state upon doping.
- Build a representative but simplified many-body hamiltonian.
- Solve model using DMFT

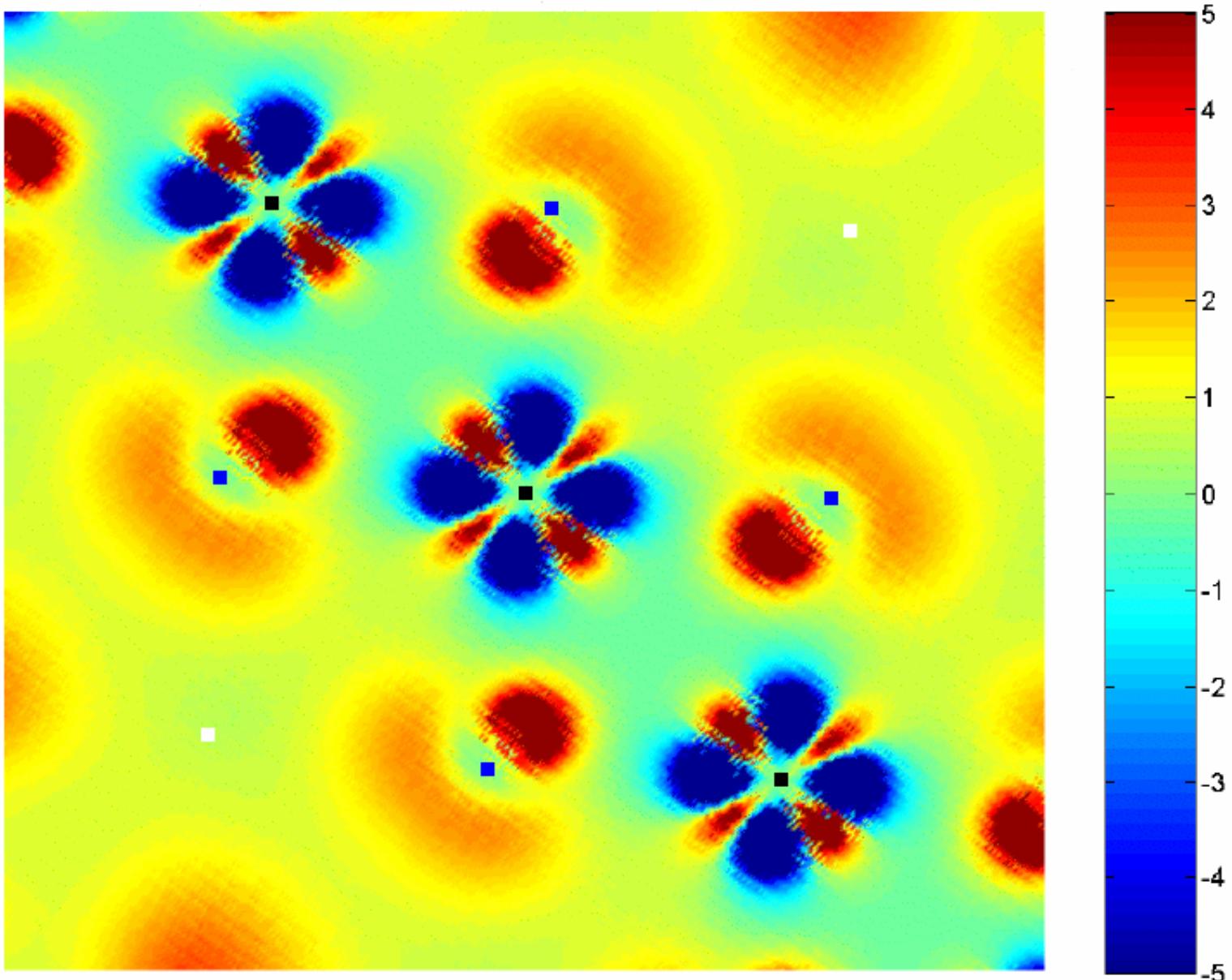
LiCoO₂ – Ordered Rock Salt



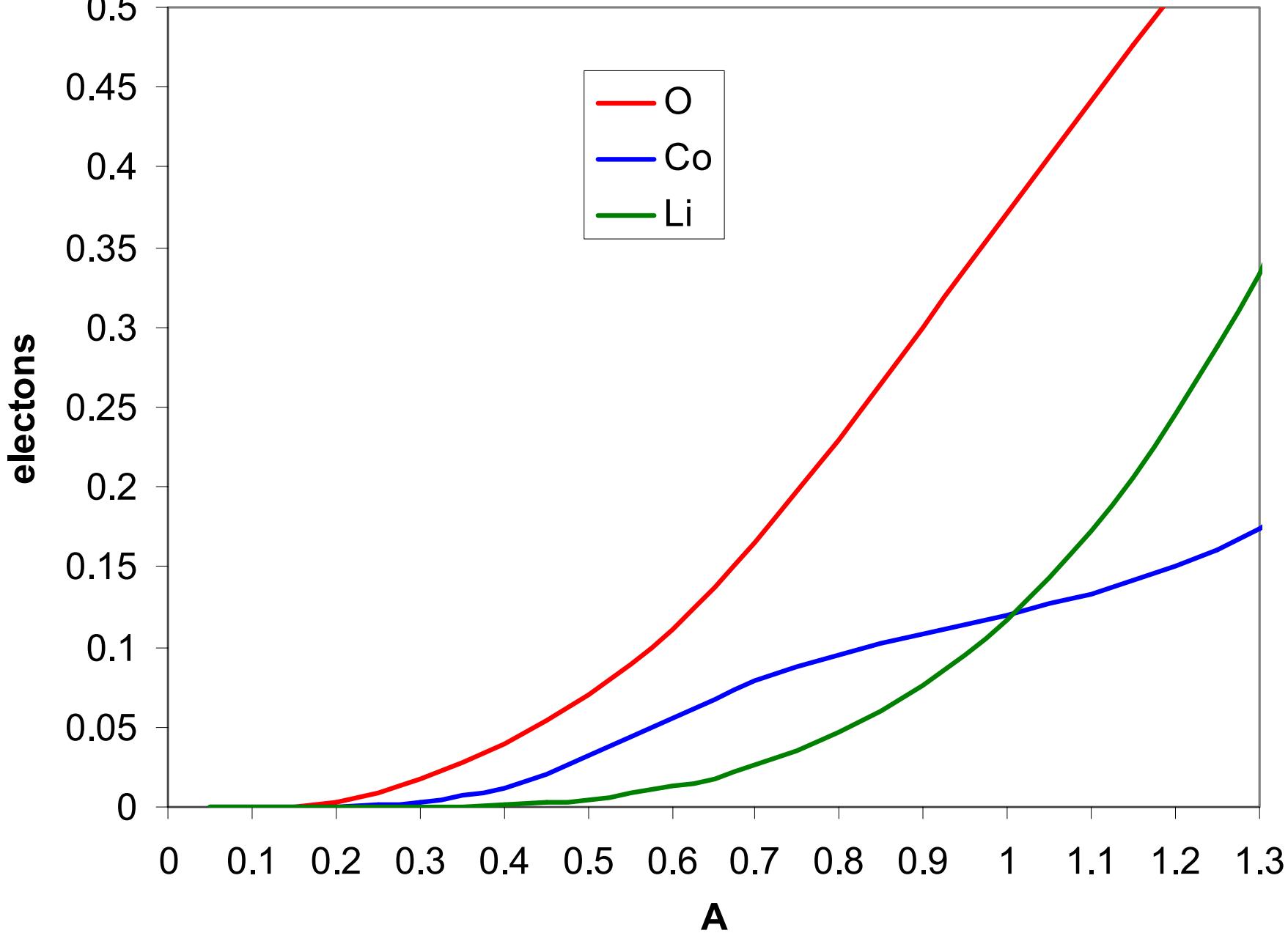
LiCoO_2 LDA DOS



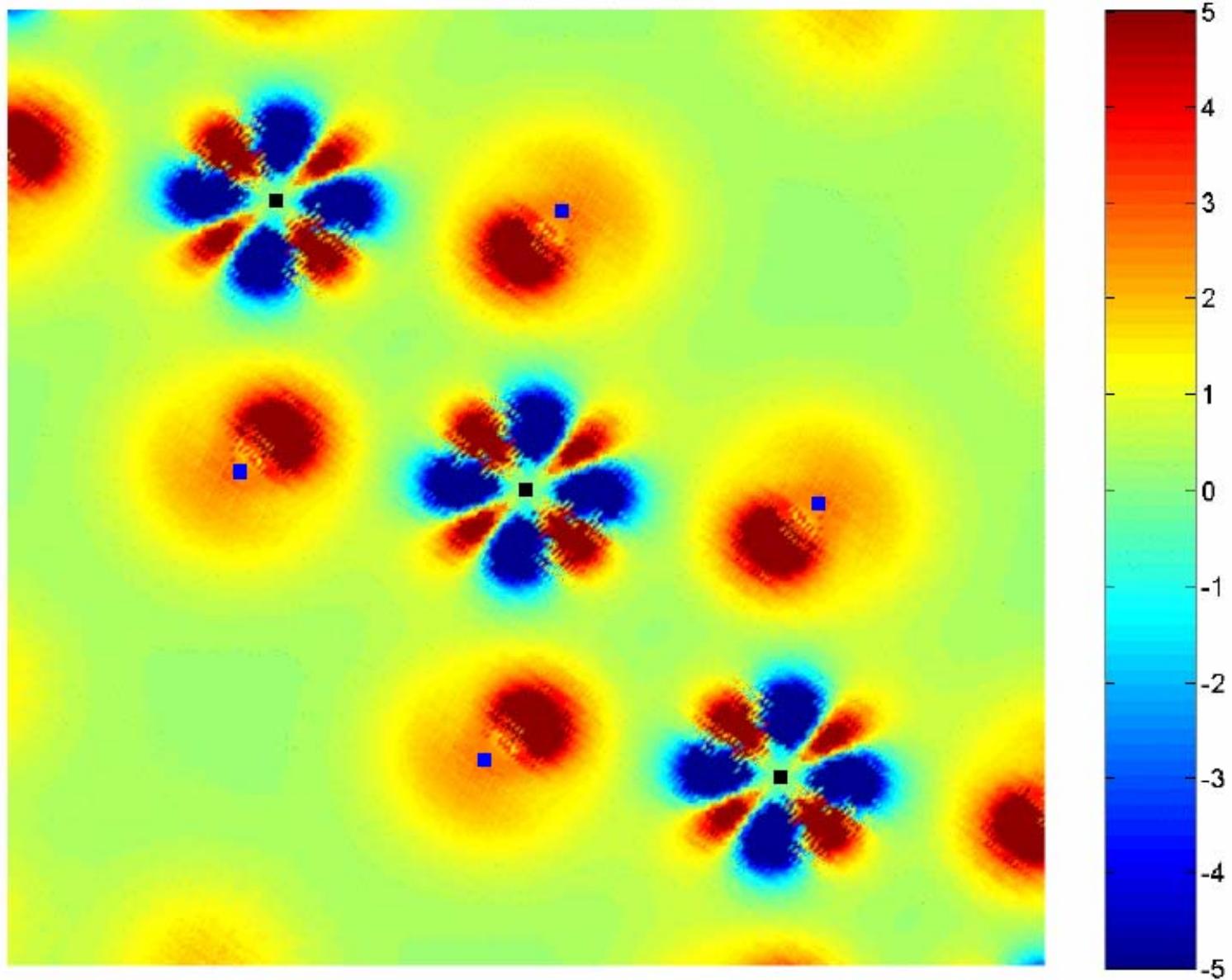
$\text{LiCoO}_2\text{-CoO}_2$ Density Difference



Electrons vs. Sphere Radius LiCoO₂ - CoO₂



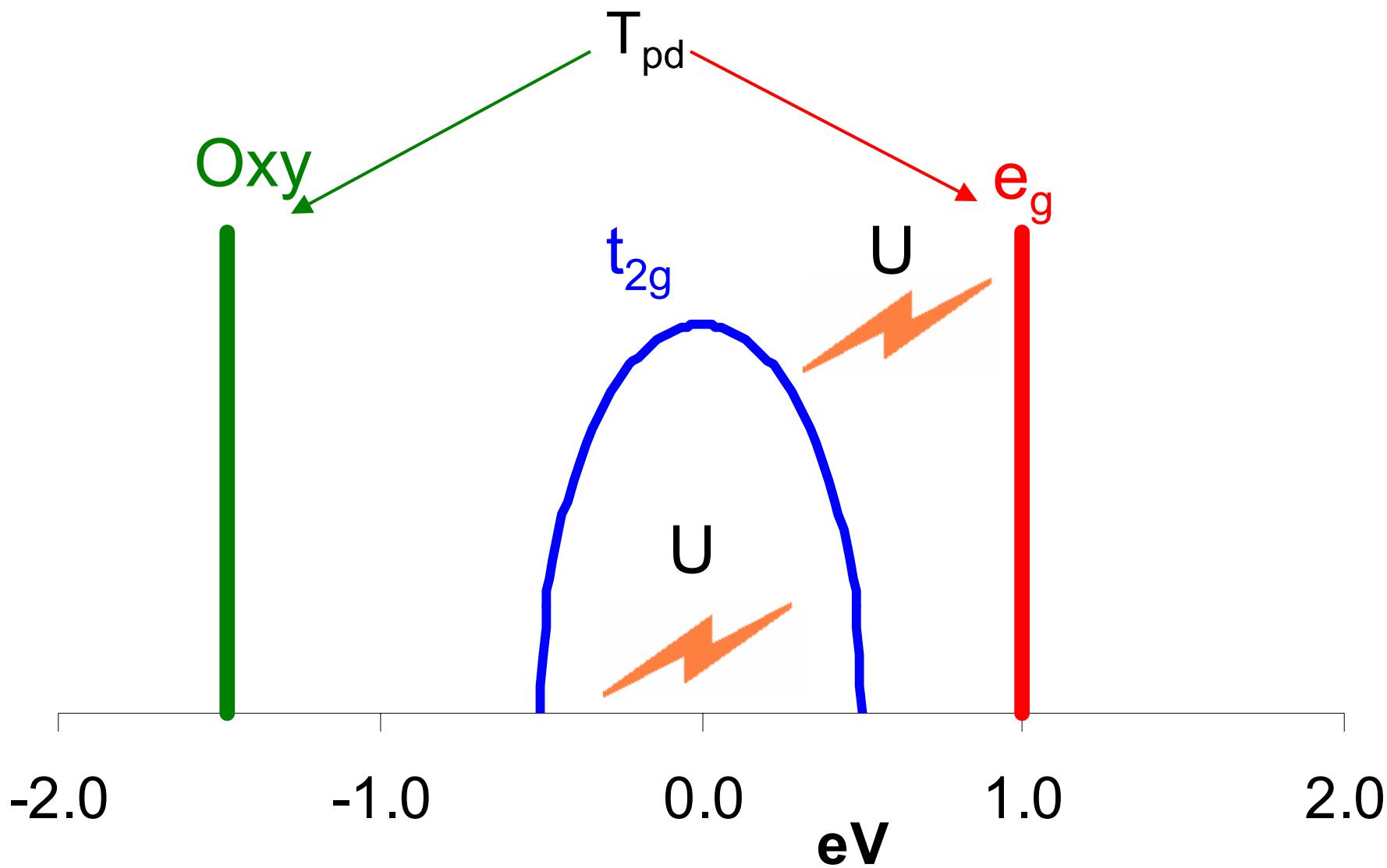
$(\text{CoO}_2 + 1e) - \text{CoO}_2$ Density Diff



Conclusions from LDA

- Particle in t_{2g} state is dressed e_g particle-hole pair.
- Nominal valence of Co changes little.
- Oxygen accepts net incoming charge.
- Mechanism is not driven by Li (Na).
- Suggests mechanism is driven by a competition between the T_{pd} and U.
- Explains high energy spectroscopy of Li_xCoO_2 .

Simple Model Hamiltonian



Simple Model Hamiltonian

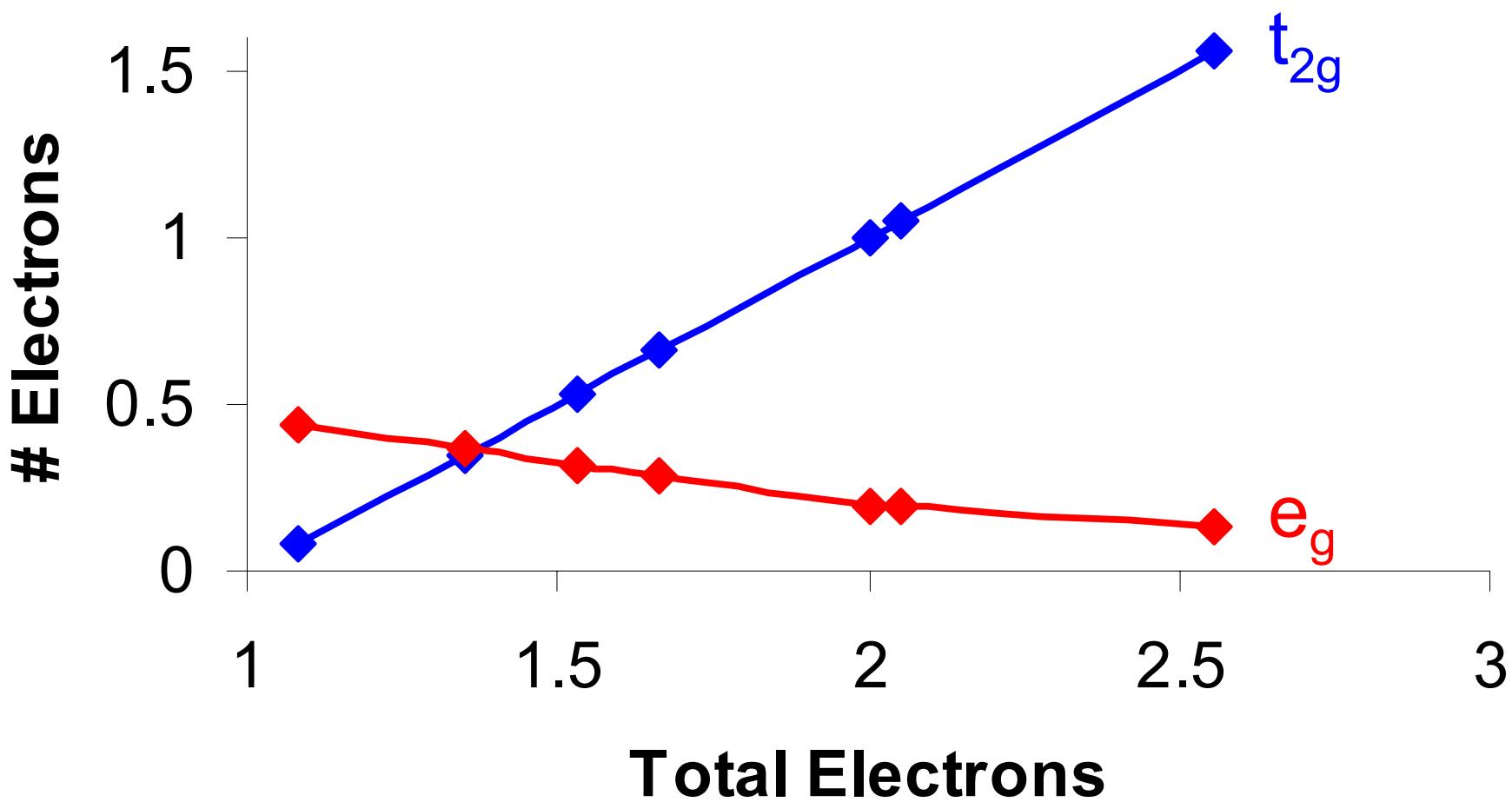
$$H = \sum_{i,\sigma} \left[\mathcal{E}_p p_{i,\sigma}^\dagger p_{i,\sigma} + \mathcal{E}_e e_{i,\sigma}^\dagger e_{i,\sigma} + T_{p-e} (e_{i,\sigma}^\dagger p_{i,\sigma} + p_{i,\sigma}^\dagger e_{i,\sigma}) \right] + \sum_{i,j,\sigma} w_{i,j} t_{i,\sigma}^\dagger t_{j,\sigma}$$

$$+ U \sum_{i,\sigma} \left[e_{i,\sigma}^\dagger e_{i,\sigma} t_{i,\sigma}^\dagger t_{i,\sigma} + t_{i,\uparrow}^\dagger t_{i,\uparrow} t_{i,\downarrow}^\dagger t_{i,\downarrow} + e_{i,\uparrow}^\dagger e_{i,\uparrow} e_{i,\downarrow}^\dagger e_{i,\downarrow} \right] - \mu \hat{N}$$

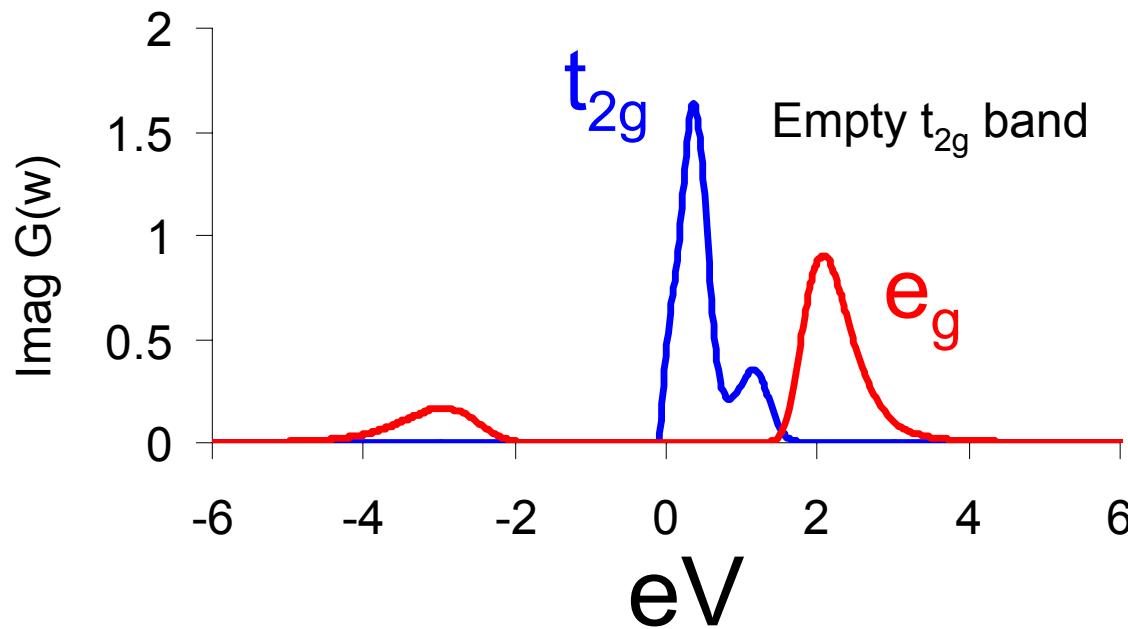
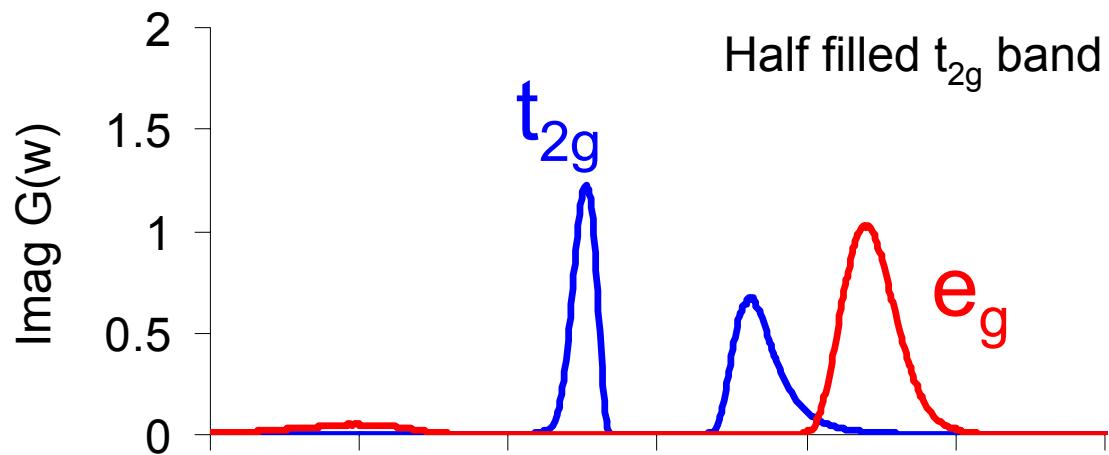
$$S_{eff} = \int_0^\beta \int_0^\beta d\tau d\tau' t^\dagger(\tau) G_t^o(\tau - \tau') t(\tau') + \int_0^\beta d\tau e^\dagger(\tau) G_e^o(\tau) e(\tau) +$$

$$U \int_0^\beta d\tau \sum_\sigma \left[e_\sigma^\dagger(\tau) e_\sigma(\tau) t_\sigma^\dagger(\tau) t_\sigma(\tau) + t_\uparrow^\dagger(\tau) t_\uparrow(\tau) t_\downarrow^\dagger(\tau) t_\downarrow(\tau) + e_\uparrow^\dagger(\tau) e_\uparrow(\tau) e_\downarrow^\dagger(\tau) e_\downarrow(\tau) \right]$$

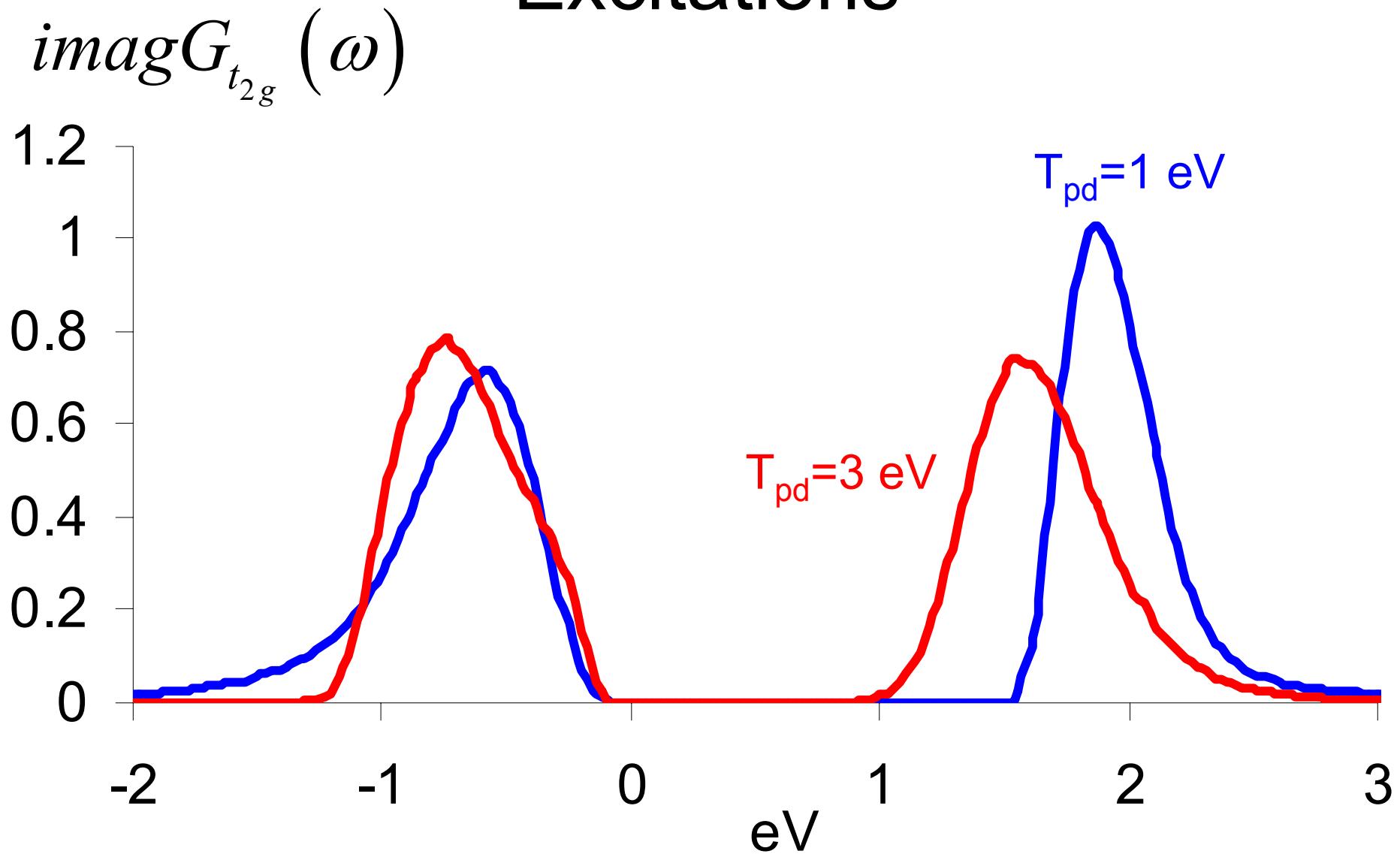
$U=3$ eV $T_{pd}=2$ eV



$U=3$ eV $T_{pd}=2$ eV



Effect of Hybridization on Excitations



Conclusions

- LDA and DMFT both produce a similar picture of rehybridization phenomena.
- Phenomena is a competition between hybridization and U.
- e_g Hybridization delocalizes t_{2g} states.
- e_g and oxygen orbitals should be considered when deriving low energy hamiltonian.
- Can we derive one-band model?